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## **Ammonia and hydrogen sulphide flux and dry deposition velocity estimates using vertical gradient method at a commercial beef cattle feedlot**

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**Abstract:** Ammonia and hydrogen sulphide flux and dry deposition velocity were estimated using micrometeorological vertical gradient flux method at a commercial cattle feedyard of approximately 50,000 head of beef cattle and average 14.4 m<sup>2</sup>/head (150 ft<sup>2</sup>/head) stocking density. Ammonia-N and H<sub>2</sub>S-S loss had general diurnal patterns with the highest fluxes in daytime and lowest fluxes in nighttime that correlated to temperature changes and active evaporation process during daytime. The highest average deposition velocities also occurred during daytime with unstable atmospheric conditions and the lowest during nighttime with very stable conditions. There are exponential relationship between NH<sub>3</sub>-N flux and ambient temperature with R<sup>2</sup> = 0.57 for NH<sub>3</sub> (NH<sub>3</sub>-N flux =  $-1.46 + 7.96e^{0.077 \cdot \text{Temperature}}$ ) and R<sup>2</sup> = 0.22 for H<sub>2</sub>S-S (H<sub>2</sub>S-S flux =  $-0.75 + 0.8e^{0.013 \cdot \text{Temperature}}$ ).

**Keywords:** ammonia; beef cattle; dry deposition; flux; gradient method; hydrogen sulphide; vertical gradient.

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## 1 Introduction

The released ammonia ( $\text{NH}_3$ ) contributes to a wide range of environmental concerns on local to international scales due to their roles as sources of fixed nitrogen to soil and plants and also to the effects of excess nitrogen on nutrient sensitive ecosystems (Aneja et al., 2001a,b; Roelle and Aneja, 2002; US EPA, 2003), but also its association with atmospheric fine particle formation (US EPA, 2003; 2004a,b). Ammonia is the most prevalent and abundant alkaline gas component in the atmosphere, and is fundamental in determining precipitation acidity (Baek and Aneja, 2004a,b; Baek et al., 2004a). The spatial scale of  $\text{NH}_3$  as a contributor to the total atmospheric nitrogen deposition is governed in part by the gas-to-particle conversion (GTPC) rate of  $\text{NH}_3$  to  $\text{NH}_4^+$ . Aneja et al., (2000) indicated that ammonia has a short lifetime due to the rapid conversion of  $\text{NH}_3$  to  $\text{NH}_4^+$  and relatively high dry deposition velocity to the surfaces near its source. However, ammonium primarily formed by GTPC processes has a longer lifetime, approximately five to ten days and could be transported for longer distances downwind from its sources. Observational data are crucial for evaluation of the  $\text{NH}_3$  emission effects from various sources, especially agricultural point and area sources. On a global scale, domestic animals have been shown to be the largest source of  $\text{NH}_3$  (Battye et al., 1994; Pain et al., 1998; Van Der Hoek, 1998). In the US, approximately 44% of total ammonia

nitrogen ( $\text{NH}_3\text{-N}$ ) emissions ( $\sim 5.3 \text{ Tg-N/year}$ ) is contributed by cattle, approximately 27% by poultry, and approximately 10% by swine in 1994 (Battye et al., 1994).

Hydrogen sulphide ( $\text{H}_2\text{S}$ ) has been known as one of the most dangerous gases in indoor buildings and in particular has caused animal as well as human deaths in animal facilities (Warneck, 2000). At 50 ppm concentrations  $\text{H}_2\text{S}$  causes dizziness, respiratory irritation, nausea and headache, and over 1000 ppm, death from respiratory paralysis can occur. Hydrogen sulphide is mainly produced by anaerobic fermentation of manure.

There are several approaches to measuring and estimating trace gas emissions from surface sources, such as

- isolation chamber and wind tunnel techniques
- micrometeorological vertical gradient and eddy correlation methods
- Gaussian dispersion and backward Lagrangian models.

The surface isolation flux chamber (Aneja et al., 2001a,b; Baek et al., 2004b; 2003; Eklund, 1992; Koziel et al., 2004; Roelle and Aneja, 2002; Schmidt, 2000) and wind tunnel (Schmidt and Bicudo, 2002; Smith and Watts, 1994) can measure trace gases from enclosed small defined areas, such as soil landfill, water and wastewater surfaces. However, micrometeorological and statistical dispersion methods are more appropriate for large surface sources with sufficient target source fetch distance and source uniformity (Flesch et al., 2002; Hutchinson et al., 1982; Oke, 1978; Phillips et al., 2004; Todd et al., 2005; Wilson et al., 1983, 2001). Due to the fact that the commercial cattle feedyards in the Texas panhandle is a large area source approximately 72 ha in size, this study conducted the vertical gradient flux (VGF) method for estimating  $\text{NH}_3$  and  $\text{H}_2\text{S}$  fluxes and dry deposition velocities.

The objectives of this study were to estimate  $\text{NH}_3\text{-N}$  and  $\text{H}_2\text{S-S}$  fluxes from a commercial feedyard in the panhandle of Texas using a micrometeorological VGF method. Since major meteorological parameters which affect trace gas emission rates from a surface are known to be surface temperature, ambient temperature, wind speed and atmospheric stability conditions, this study also investigated the relationships of  $\text{NH}_3\text{-N}$  and  $\text{H}_2\text{S-S}$  fluxes, and dry deposition velocities with meteorological variables (ambient temperature and manure temperature) and atmospheric stability classes.

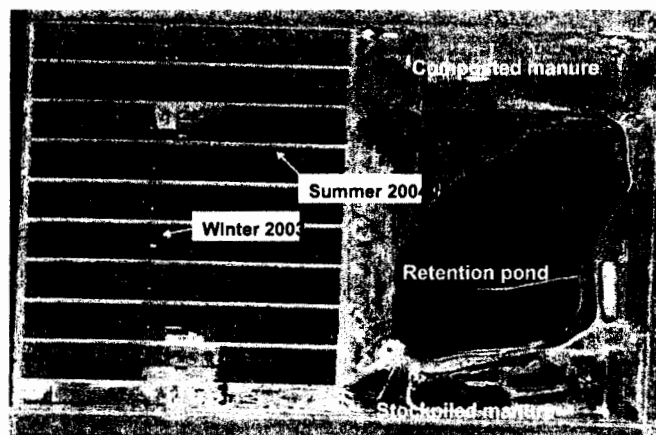
## **2 Methodology**

### *2.1 Sampling location and scheme*

Two observations of  $\text{NH}_3\text{-N}$  and  $\text{H}_2\text{S-S}$  fluxes and dry deposition velocities using micrometeorological VGF method were conducted at a commercial cattle feedyard in the Texas panhandle from 22nd to 24th January 2003 and 16th June to 6th July 2004. The operation accommodated approximately 50,000 head of beef cattle with an average of  $14.4 \text{ m}^2/\text{head}$  ( $150 \text{ ft}^2/\text{head}$ ) stocking density. In order to estimate  $\text{NH}_3\text{-N}$  and  $\text{H}_2\text{S-S}$  fluxes and dry deposition velocities using the VGF method, time-resolved trace gas concentrations and meteorological parameters in the horizontally homogeneous atmospheric surface layer are necessary (Arya, 1999). However, the feedyard surface contains 1.5-m tall pen fences, beef cattle, their irregular daily activities, manure banks in

the centre of pens, and several buildings including an office, feed mills, hospital and roping area within the feedyard. In addition there are: a retention pond, manure stockpiles and composted manure area (Figure 1). Considering the fetch distance in the direction of winds and to reduce the potential interference of emissions from other potential sources (a retention pond and stockpiles), the tower was located within a feedyard. The tower for the winter 2003 event was located in the centre quadrant and, for the summer 2004 event, the tower was re-located in the northeastern quadrant area of the yard to maximise fetch in the direction of the prevailing southwesterly winds (Figure 1). We excluded observations when the wind was from other than  $180^{\circ}$  to  $270^{\circ}$ . A total of 29 hourly average  $\text{NH}_3$  and  $\text{H}_2\text{S}$  measurements were selected for the 2003 winter experiment and a total of 83 and 122 hourly average  $\text{NH}_3$  and  $\text{H}_2\text{S}$  measurements were selected for the 2004 summer experiment, respectively (Table 1). Wind direction and wind speed at 8 m, relative humidity, precipitation, manure temperature and net radiation were also monitored at a co-located weather tower.

**Figure 1** Schematic of sampling location at a commercial feedyard in Texas



Ambient  $\text{NH}_3$  and  $\text{H}_2\text{S}$  were measured continuously at 3-m and 6-m heights and profiles of wind speed (WS) and ambient temperature were monitored at a 10-m weather tower. Ammonia concentrations were measured with a Thermo Environment Instrument (TEI) 17C chemiluminescence  $\text{NH}_3$  analyser (Franklin, MA) with a range of 0 to ten parts per million by volume (ppmv). Hydrogen sulphide concentrations were measured in real time with a pulsed fluorescence  $\text{SO}_2$  detector (TEI Model 45C) after  $\text{H}_2\text{S}$  was converted to  $\text{SO}_2$  by a converter (TEI Model 340). In order to measure trace gas concentrations at two different heights, a three-way solenoid was installed to switch the gas sampling line from one height to the other every ten minutes. Due to the response time of each analyser unit, only the last three minutes of each ten minutes sampling period, was used at each height concentration. The three minute averages occurring every 20 minutes per height were then averaged for hourly average trace gas concentrations.

**Table 1** Hourly averages of ambient temperatures, wind speed, ammonia and hydrogen sulphide concentrations measured at two heights (3-m and 6-m),  $\text{NH}_3$ -N and  $\text{H}_2\text{S}$ -S flux estimates ( $F_c$ ) from this study,  $F_{\text{air}}$  and  $F_{\text{flux}}$  and stability classes

NH <sub>3</sub>	Temp.	Temp.	WS	WS	[NH <sub>3</sub> ]	[NH <sub>3</sub> ]	[NH <sub>3</sub> ]	NH <sub>3</sub> -N Flux	NH <sub>3</sub> -N Flux	NH <sub>3</sub> -N Flux	NH <sub>3</sub> -N Flux	NH <sub>3</sub> -N Dry	R <sub>i</sub>	z <sub>a</sub> /L	u*
Summer	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
(6/16/2004)	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
Min	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
DF <sup>2</sup>	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
2003	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
Winter	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
(1/23/2003)	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
Min	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
DF	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
2004	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
Summer	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
(6/16/2004)	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
Min	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
DF	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
2003	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
Winter	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
(1/23/2003)	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
Min	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*
DF	3-m	6-m	3-m	6-m	3-m	6-m	3-m	(F <sub>c</sub> )	(F <sub>air</sub> )	(F <sub>flux</sub> )	(F <sub>flux</sub> )	Deposition	R <sub>i</sub>	z <sub>a</sub> /L	u*

Notes: STD<sup>1</sup>: Standard Deviation; DF<sup>2</sup>: Degree of Freedom

Diet samples from feed bunks and samples of dry unconsolidated manure surface were sampled by the US Department of Agriculture-Agricultural Research Service (USDA-ARS) in Bushland, TX. Diet and pen surface samples were analysed for nitrogen mass balance study using a N:P ratio (Todd et al., 2005). Trace gas analysers were housed in a temperature-controlled mobile laboratory. The mobile system consisted of a modified 5 ft × 7 ft sized trailer with a 13,500 BTU air-conditioning unit. A Campbell Scientific data logger 23 x was used as an automated data acquisition system and recorded 60-s rolling average measurements. Data were downloaded daily.

## 2.2 Vertical gradient flux (VGF) method

The micrometeorological VGF method is one of the most widely used for trace gas vertical flux estimations for large surface sources. It is an analogy between molecular and turbulent exchange processes based on eddy diffusivity relations. Under the assumption of the same eddy diffusivity for gaseous mass and heat, the mean VGF ( $F_c$ ) could be expressed as:

$$F_c = -K_m \frac{\partial \bar{c}}{\partial z} \equiv -K_h \frac{\partial \bar{c}}{\partial z}, \quad (1)$$

where  $\delta \bar{c}$  is the difference between the mean concentrations at the two different heights ( $z_1$  and  $z_2$ ).  $K_m$  and  $K_h$  are the eddy diffusivities of mass and heat involving mean gradients, respectively. Eddy diffusivities can be expressed in terms of the Monin-Obukhov (M-O) similarity functions for momentum and heat flux,  $\phi_m(\zeta)$  and  $\phi_h(\zeta)$ , respectively (Equation 1). The friction velocity ( $u_*$ ) is related to air-surface stress,  $k$  is the von Karman constant (assumed to be  $k \approx 0.4$ ), and  $\delta u$  is the difference between the mean wind velocity at the two different heights ( $z_1$  and  $z_2$ ) (Equation 2).

$$\frac{K_h}{kzu_*} = \frac{1}{\phi_h(\zeta)} \left( u_* = \frac{kz}{\phi_m} \frac{\partial \bar{u}}{\partial z} \right) \equiv \left( \frac{k}{\phi_m} \frac{\Delta \bar{u}}{\ln(z_2/z_1)} \right) \quad (2)$$

By substituting Equation 2 into Equation 1, the VGF ( $F_c$ ) can be determined by the following equation:

$$F_c = \overline{w'c'} = -\frac{kzu_*}{\phi_h} \frac{\partial \bar{c}}{\partial z} \equiv \frac{ku_*}{\phi_h} \frac{\Delta \bar{c}}{\ln(z_2/z_1)} \quad (3)$$

The empirical M-O similarity functions for momentum and heat flux are determined from micrometeorological experiments in various flat and homogeneous surfaces. The most widely used and simplest forms from Businger-Dyer relations are (Arya, 1995, 1999):

$$\phi_h = \phi_m^2 = (1 - 15\zeta)^{-1/2}, \quad \text{for } -5 < \zeta < 0 \text{ (Unstable)} \quad (4)$$

$$\phi_h = \phi_m = 1 + 5\zeta, \quad \text{for } 1 > \zeta \geq 0 \text{ (Stable)} \quad (5)$$

$\zeta = z_m/L$  can be also determined by its relationship to  $R_i(z_m)$  estimated from Equation 6.  $L$  is the M-O length which is the depth of the near-surface layer in which shear effects are likely to be significant under any stability conditions.  $z_m$  is a geometric mean height ( $z_m = \sqrt{z_1 z_2}$ ). The corresponding relations between  $\zeta = z_m/L$  and  $R_i(z_m)$  are (Arya, 1999):

$$R_i(z_m) = \frac{g}{T_o} \frac{\partial \bar{\theta} / \partial z}{(\partial \bar{u} / \partial z)^2} \equiv \frac{g}{T_o} \frac{\Delta \bar{\theta} z_m}{(\Delta \bar{u})^2} \ln \left( \frac{z_2}{z_1} \right) \quad (6)$$

$$\zeta = R_i \text{ for } R_i < 0 \quad (7)$$

$$\zeta = \frac{R_i}{1 - 5R_i}, \text{ for } 0 \leq R_i < 0.2. \quad (8)$$

The direct quantitative measurements of vertical gaseous mass flux near the surfaces can be used for the purpose of characterising the dry deposition velocity ( $V_d$ ) commonly used in the parameterisation of dry deposition rates which can be expressed as:

$$V_d = -\frac{F_c}{c}, \quad (9)$$

where  $\bar{c}$  is the mean concentration at the reference height above the surface e.g. the canopy or roughness layer. In general, vertical flux is assumed to be positive when it is directed upward from a source, and dry deposition velocity is assumed to be negative as it is directed down, toward the surface.

### 3 Results and discussion

For the summer 2004 experiment, the mean  $\text{NH}_3\text{-N}$  flux estimated using the VGF method was  $3671 \pm 2624 \mu\text{g NH}_3\text{-N/m}^2/\text{min}$  (Table 2). This flux estimate was significantly higher than  $\text{NH}_3\text{-N}$  fluxes measured during the summer of 2003 at the same feedyard using the isolation chamber method (Baek et al., 2004b; Koziel et al., 2004). During the summers of 2003 and 2002 the mean  $\text{NH}_3\text{-N}$  flux from the feedyard surface using the chamber method was  $1666 \pm 1642$  and  $1681 \pm 1931 \mu\text{g NH}_3\text{-N/m}^2/\text{min}$ , respectively. In contrast to the summer measurements, the winter measurements were conducted within the same season and were scheduled as a series. During the winter 2003 experiment, the isolation chamber method (8–21 January 2003) was conducted for 13 days (Koziel et al., 2004) and the VGF method (22–24 January 2003) was conducted for 2.5 days. The mean flux measured with the chamber method during the 2003 winter campaign was  $289 \pm 237 \mu\text{g NH}_3\text{-N/m}^2/\text{min}$ . The ammonia flux estimate using the VGF method was  $317 \pm 209 \mu\text{g NH}_3\text{-N/m}^2/\text{min}$ . The difference between the ammonia-N flux estimates was approximately 11.6%. This difference is quite small considering how different these two methodologies are and the uncertainties associated with them (Table 2). Mean  $\text{NH}_3\text{-N}$  emission rate ( $329 \text{ kg NH}_3\text{-N}\cdot\text{d}^{-1}$ ) in winter 2003 were much lower than in summer 2004 ( $3795 \text{ kg NH}_3\text{-N}\cdot\text{d}^{-1}$ ) due mainly to significant lower manure temperature in winter time.

**Table 2** Comparison of average  $\text{NH}_3\text{-N}$  and  $\text{H}_2\text{S-S}$  fluxes between using VGF and isolation chamber at the commercial cattle feedyard in the Texas panhandle

Reference	Measurement period	Sampling technique	Site description	$\text{NH}_3\text{-N}$ flux ( $\mu\text{g}/\text{m}^2/\text{min}$ )	$\text{H}_2\text{S-S}$ flux ( $\mu\text{g}/\text{m}^2/\text{min}$ )
This study	Winter 2003	VGF	Commercial Cattle Feedyard, Texas	$317 \pm 209$	$-0.99 \pm 2.91$
	Summer 2004			$3671 \pm 2624$	$21.71 \pm 20.71$
Koziel et al. (2004)	Summer 2002	Dynamic isolation		$1666 \pm 1642$	$1.28 \pm 1.06$
	Winter 2003	flux		$289 \pm 237$	$0.31 \pm 0.63$
	Summer 2003	chamber		$1681 \pm 1931$	$1.22 \pm 1.08$

In general, N may volatilise as gaseous nitrogen such as  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , NO and  $\text{NO}_2$  unlike phosphorous (P) from the feedyard surface. Thus, a change in the N:P ratio between feed and manure could be an indicator of the total N volatilisation losses from the manure surface due to N retention by the animal. Todd et al. (2005) reported that 54% fed N was lost to volatilisation during the same 2004 summer campaign and indicated that most N intake is lost as  $\text{NH}_3$  into atmosphere.

The estimates of  $\text{H}_2\text{S-S}$  flux using the VGF method were considerably higher ( $21.71 \pm 20.71 \mu\text{g H}_2\text{S-S}/\text{m}^2/\text{min}$ ) during the 2004 summer campaign than downward deposition flux ( $-0.99 \pm 2.91 \mu\text{g H}_2\text{S-S}/\text{m}^2/\text{min}$ ) during the 2003 winter campaign. During the 2004 summer experiment, five rain events including two thunderstorms were recorded. The significantly higher  $\text{H}_2\text{S}$  fluxes were observed the following day after the rainfall due to active evaporation processes by manure temperature increase. These results are consistent with Baek et al. (2004) results using the chamber method. The negative deposition flux contradicts our current knowledge about the fate of  $\text{H}_2\text{S}$  emissions at a commercial feedyard. One explanation could be the relatively high standard deviation associated with the very low flux measurements (Table 2). Hydrogen sulphide-S emission rates during the 2004 summer campaign averaged  $22.5 \text{ kg H}_2\text{S-S}\cdot\text{d}^{-1}$ .

### 3.1 Comparison of empirical VGF formulae

Important factors in the application of the VGF method are surface land use type and geographical location, which are related to diffusivities of mass, momentum and heat, stability class and turbulence. In order to determine these micrometeorological parameters, it is necessary to have some experimental input to an approximate or incomplete theory to develop useful empirical relationships between turbulent fluxes, mean gradient and stability classes. There are many studies conducted which improve and/or develop the empirical gradient formula based on the gradient transport theories and similarity theories and can be applied to a variety of sources (Arya, 1999; Duyzer et al., 1992; Flesch et al., 2002; Fowler et al., 2001; Oke, 1978; Phillips et al., 2004; Sutton et al., 2000; Wilson et al., 1983; 2001). First-order closure K-theory is still widely used in applications to air pollution transport. Similarity theory is known as a more sophisticated theory based on dimensional analysis to develop the relationships between variables mentioned earlier.



Flesch et al. (2002) applied the turbulent Schmidt number ( $Sc$ : the ratio of eddy diffusivity for momentum to the diffusivity for trace mass  $\approx 0.6$ ) for the measurement of trace gas emissions. Because of the higher uncertainty of conventional diffusivity of trace gas, they indicated that conventional VGF methods underestimated the true trace gas emission. In this present study, we compared ammonia and hydrogen sulphide flux with Flesch et al.'s (2002) vertical gradient formula based on their Schmidt number application. Conventional VGF ( $F_{Oke}$ ) from Oke (1978) and Flesch's VGF ( $F_{Flesch}$ ) from Flesch et al. (2002) are expressed as:

$$F_{Oke} = -\frac{k^2}{\phi_m \phi_c} \frac{z_m^2}{\partial z^2} \partial \bar{c} \partial \bar{u} \quad (10)$$

$$F_{Flesch} = -\frac{k^2}{Sc \phi_m^2} \frac{z_m^2}{\partial z^2} \partial \bar{c} \partial \bar{u}, \quad (11)$$

where  $Sc = 0.6$  recommended by Flesch et al. (2002) for the atmospheric surface layer based on empirical experiments. He determined M-O similarity functions for momentum and mass flux,  $\phi_m(\zeta)$  and  $\phi_c(\zeta)$ , respectively from and Dyer and Bradley (1982), and M-O length ( $L$ ).

$$L = \frac{z_m}{0.67 R_i} \quad \text{for Unstable } (R_i < 0) \quad (12)$$

$$L = \frac{z_m}{R_i (1 - 5 R_i)} \quad \text{for Stable } (R_i > 0) \quad (13)$$

$$\phi_m = 1 + \frac{4.8 z_m}{L} \quad \text{and} \quad \phi_c = 0.95 + \frac{4.5 z_m}{L} \quad \text{for Stable } (L > 0) \quad (14)$$

$$\phi_m = \left(1 - \frac{15 z_m}{L}\right)^{-1/4} \quad \text{and} \quad \phi_c = 0.95 \left(1 - \frac{14 z_m}{L}\right)^{-1/2} \quad \text{for Unstable } (L < 0) \quad (15)$$

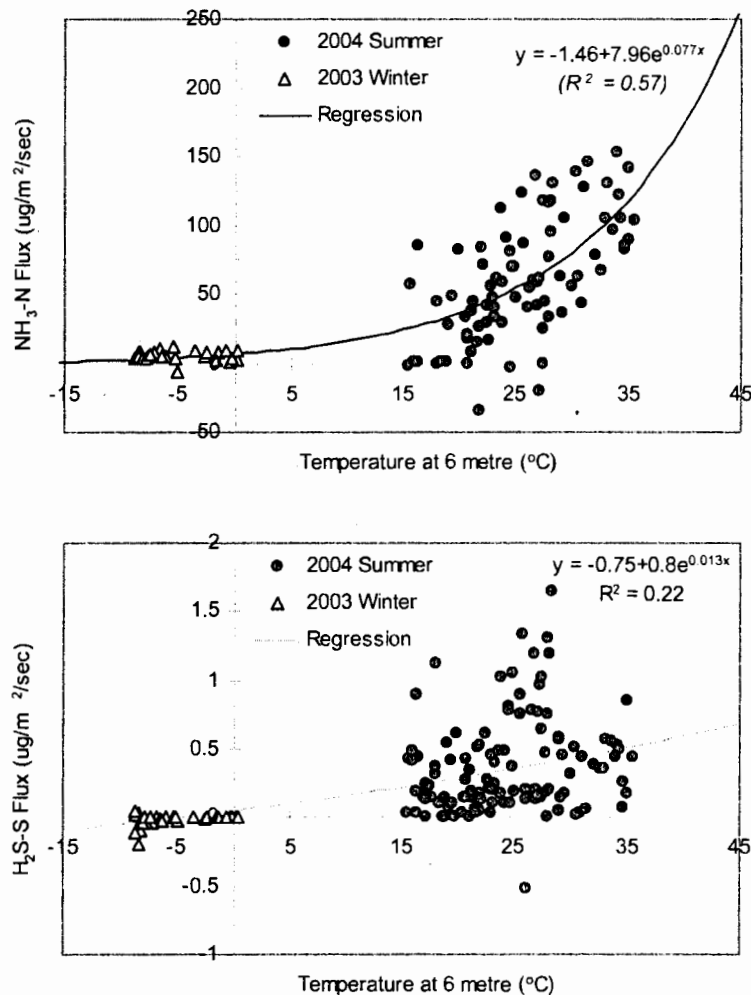
Table 1 indicates that  $\text{NH}_3$ -N flux estimated by Oke (1978) ( $F_{Oke}$ ) and Flesch et al. (2002) ( $F_{Flesch}$ ) are approximately 20 and 60% higher than  $\text{NH}_3$ -N flux estimate ( $F_c$ ) in this study, respectively. The main reason for the significant discrepancy between ( $F_{Flesch}$ ) and ( $F_c$ ) is caused by the Schmidt number ( $Sc$ ) of approximately 0.6.

Figures 2 and 3 show diurnal variations in  $\text{NH}_3$ -N and  $\text{H}_2\text{S}$ -S fluxes ( $F_c$ ), Oke (1978)  $\text{NH}_3$ -N flux ( $F_{Oke}$ ) and Flesch et al. (2002)  $\text{NH}_3$ -N flux ( $F_{Flesch}$ ) during the 2004 summer experiment. Ammonia and hydrogen sulphide flux have general diurnal patterns with higher flux in the daytime and lower flux at night time, probably due to manure/soil temperature changes and active evaporation process during the daytime. It clearly appears that  $\text{NH}_3$ -N and  $\text{H}_2\text{S}$ -S fluxes estimated by  $F_{Flesch}$  are greater than  $F_c$  and  $F_{Oke}$  and the magnitude of discrepancy is greater during the daytime than at night time.

diurnal trend as  $\text{NH}_3\text{-N}$  flux estimates and was positively correlated with  $\text{NH}_3\text{-N}$  fluxes ( $R^2 = 0.56$ ) and  $\text{H}_2\text{S-S}$  fluxes ( $R^2 = 0.70$ ). This finding is consistent with strong correlations between manure temperature and flux for three seasons reported earlier (Koziel et al., 2004). Hydrogen sulphide also had the same trends as ammonia flux.

Due to the absence of manure temperature observations for the 2003 Winter campaign, we determined the exponential relationship between  $\text{NH}_3\text{-N}$  flux and temperature at 6-m including both experiments (winter 2003 and summer 2004) with  $R^2 = 0.57$  for  $\text{NH}_3$  ( $\text{NH}_3\text{-N flux} = -1.46 + 7.96e^{0.077 \cdot \text{Temperature}}$ ) and  $R^2 = 0.22$  for  $\text{H}_2\text{S-S}$  ( $\text{H}_2\text{S-S flux} = -0.75 + 0.8e^{0.013 \cdot \text{Temperature}}$ ) (Figure 4). These results suggest that  $\text{NH}_3\text{-N}$  flux is well-correlated to ambient temperature at 6-m in this study.

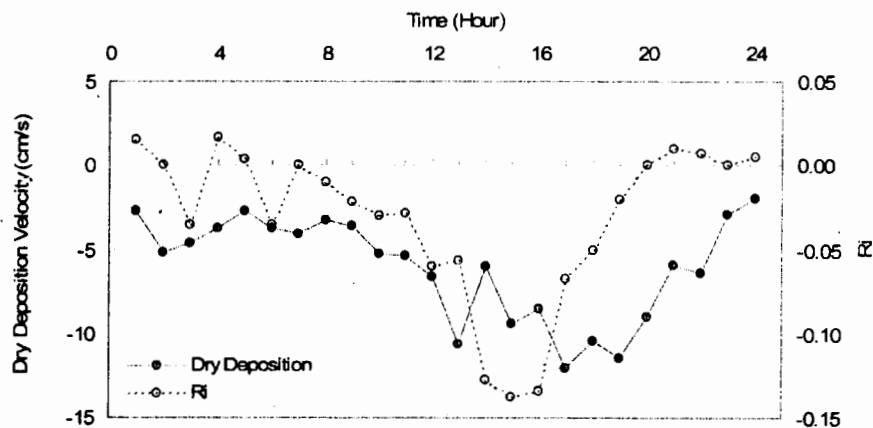
**Figure 4** Correlation of  $\text{NH}_3\text{-N}$  and  $\text{H}_2\text{S-S}$  flux from this study ( $F_c$ ) with ambient temperature at 6-m during winter 2003 and summer 2004 experiments



### 3.2 Dry deposition velocity and atmospheric stability

Atmospheric stability during experiments was determined by the Richardson number ( $R_i$ ) and M-O stability parameter  $\zeta = z_m/L$ . During the winter 2003 and summer 2004 experiments, most hourly stability conditions ranged from unstable to very unstable ( $R_i \leq 0$ ). Mean  $R_i$  values from summer and winter in this study were  $-0.04 \pm 0.07$  during the summer 2004 experiment (maximum = 0.06) and  $-0.03 \pm 0.03$  during the winter 2003 experiment (maximum =  $-0.01$ ) (Table 1). Deposition velocity was calculated here as the ratios of the flux to mean concentrations measured at 3-m (Equation 9). Mean dry deposition velocity ( $V_d$ ) for  $\text{NH}_3\text{-N}$  and  $\text{H}_2\text{S-S}$  during the summer of 2004 were  $-6.27 (\pm 4.47)$  cm/sec and  $-7.32 (\pm 5.34)$  cm/sec, respectively. The diurnal variations in ammonia  $V_d$  and stability  $R_i$  during summer 2004 had similar patterns (Figure 5). The highest average  $V_d$  occurred during the daytime under very unstable atmospheric conditions and the lowest during the night time under neutral and stable atmospheric conditions. There was a strong correlation between  $V_d$  and  $R_i$  ( $R^2 = 0.74$  for  $\text{NH}_3\text{-N}$  flux;  $R^2 = 0.55$  for  $\text{H}_2\text{S-S}$  flux).

**Figure 5** Diurnal variations in  $\text{NH}_3\text{-N}$  dry deposition velocity ( $V_d$ ) and stability class Richardson number ( $R_i$ ) during summer 2004



## 4 Conclusion

The micrometeorological VGF method has been known as the most comprehensive method to reasonably estimate ammonia fluxes from a large surface area, e.g. a commercial cattle feedyard. Ammonia-N emission rates averaged approximately 3795 kg  $\text{NH}_3\text{-N/day}$  during the summer 2004 experimental period and 329 kg  $\text{NH}_3\text{-N/day}$  during the 2003 winter period. The mean  $\text{H}_2\text{S-S}$  emission rate was 22.5 kg  $\text{H}_2\text{S-S/day}$  during the 2004 summer period. Ammonia and  $\text{H}_2\text{S-S}$  loss had general diurnal patterns with the highest fluxes in the daytime and lowest fluxes at night time that correlated to manure temperature changes and active evaporation process during the daytime. The highest average deposition velocities also occurred during the daytime with unstable atmospheric conditions and the lowest values during the night time with very stable conditions.

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